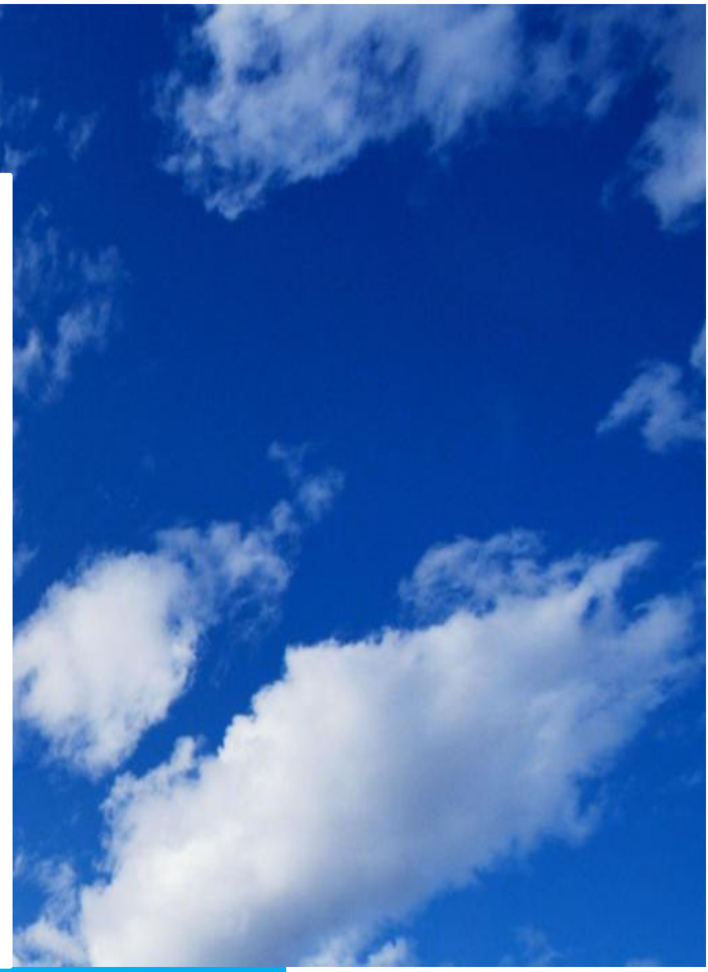


# OZONE ($O_3$) INSTRUMENTS

Ozone is a critical pollutant causing health risks and needs to be monitored using specialized instrumentation.

South African Weather Service

# What is Ozone

Ozone, or trioxygen, is an inorganic molecule with the chemical formula $O_3$. It is a pale blue gas with a distinctively pungent smell. Ozone is formed from dioxygen by the action of ultraviolet (UV) light and electrical discharges within the Earth's atmosphere. It is present in very low concentrations throughout the latter, with its highest concentration high in the ozone layer of the stratosphere, which absorbs most of the Sun's ultraviolet (UV) radiation.

**Definition**

Ozone is an inorganic molecule with the chemical formula O3.

It is a toxic gas and the odour is reminiscent of chlorine, and detectable by many people at concentrations of as little as 0.1 ppm in air. $O_3$ is a very strong oxidizing agent.

The chemical composition of Ozone is written as $O_3$ which tells us that this gas consists of three Oxygen molecules.

$$O_2 + O \rightarrow O_3$$

$O_3$ is a bent molecule with $C_{2v}$ symmetry (similar to the water molecule). The O - O distances are 127.2 pm (1.272 Å) and the O - O - O angle is 116.78°.

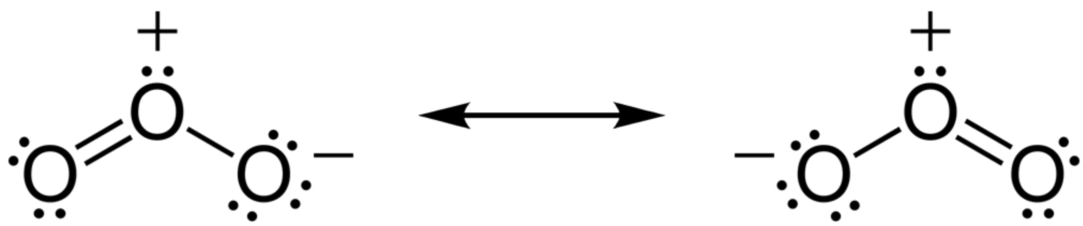



Figure 6.1: Representation of the two resonance structures of $O_3$.

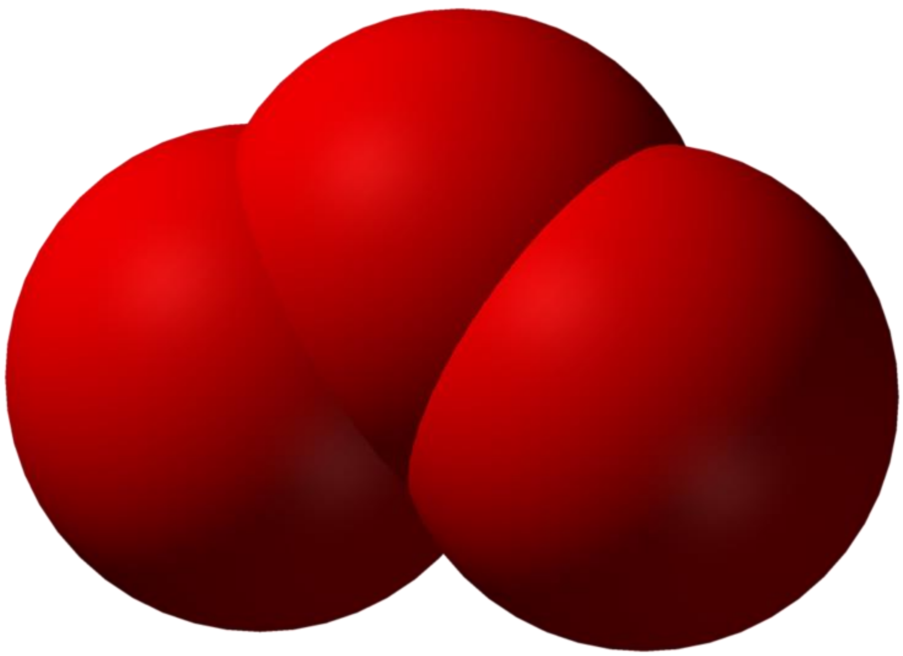


Figure 6.2: 3D representation of the chemical composition of $O_3$.

# How do we measure $O_3$

The measurement of Ozone ($O_3$) in air is based on UV absorption analysis or UV spectroscopy.

**Definition**
UV spectroscopy is type of absorption spectroscopy in which light of ultra-violet region (200-400 nm) is absorbed by the molecule which results in the excitation of the electrons from the ground state to higher energy state

To enable us to measure trace levels of $O_3$ in ambient air we also make use of the principles of UV spectroscopy and certain components are required inside an instrument to do so. These basic components include:

- Electrical circuits to power the sensors and other circuits.
- Electronic circuits to measure voltages from sensors and circuits.
- Processor that can perform calculations and display data.
- Source that can emit ultraviolet light.
- Optical bench for the absorption to take place without interference.
- Sensor that can measure the remaining UV light.

Although several different type of $O_3$ analysers are available on the market and they are all manufactured by different suppliers most instruments make use of the same basic components and principle to measure $O_3$ in ambient air. To understand the principle of UV absorption/spectroscopy we first need to look at how ultraviolet light affects the $O_3$ molecules.

# What is Ultraviolet light and how do we measure it?

Light is measured by its wavelength (in nanometers) or frequency (in Hertz). One wavelength equals the distance between two successive wave crests or troughs. Frequency (Hertz) equals the number of waves that passes a given point per second.

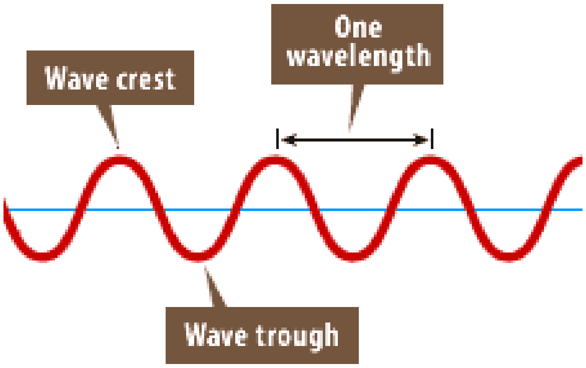



Figure 6.3: Light is measured in wavelength or frequency.

**Definition**
In physics, the wavelength is the spatial period of a periodic wave—the distance over which the wave's shape repeats.

**Definition**
Frequency is the number of occurrences of a repeating event per unit of time. It is also referred to as temporal frequency, which emphasizes the contrast to spatial frequency and angular frequency.

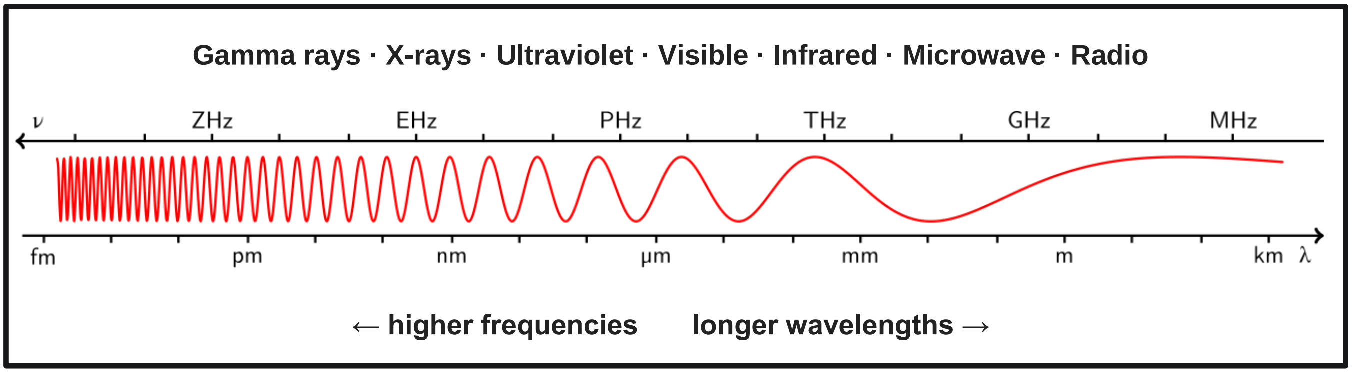



Figure 6.4: The full electromagnetic spectrum.

Light is measured at different wavelengths in nanometres, the electromagnetic spectrum for light is the available range of light that we can measure, the spectrum starts at a wavelength of 200 nM up to 20 µM. Ultraviolet light which is used for UV spectroscopy and which helps us to measure $O_3$ starts from 200 nM up to 400 nM, the visible light spectrum (VIS) that we see as colors is from 400 nM up to 700 nM. The next range of light is near infrared (NIR) which is measured from 700 nM up to 2 µM and the last spectrum of light is infrared light (IR) which is measured from 2 µM up to 20 µM.

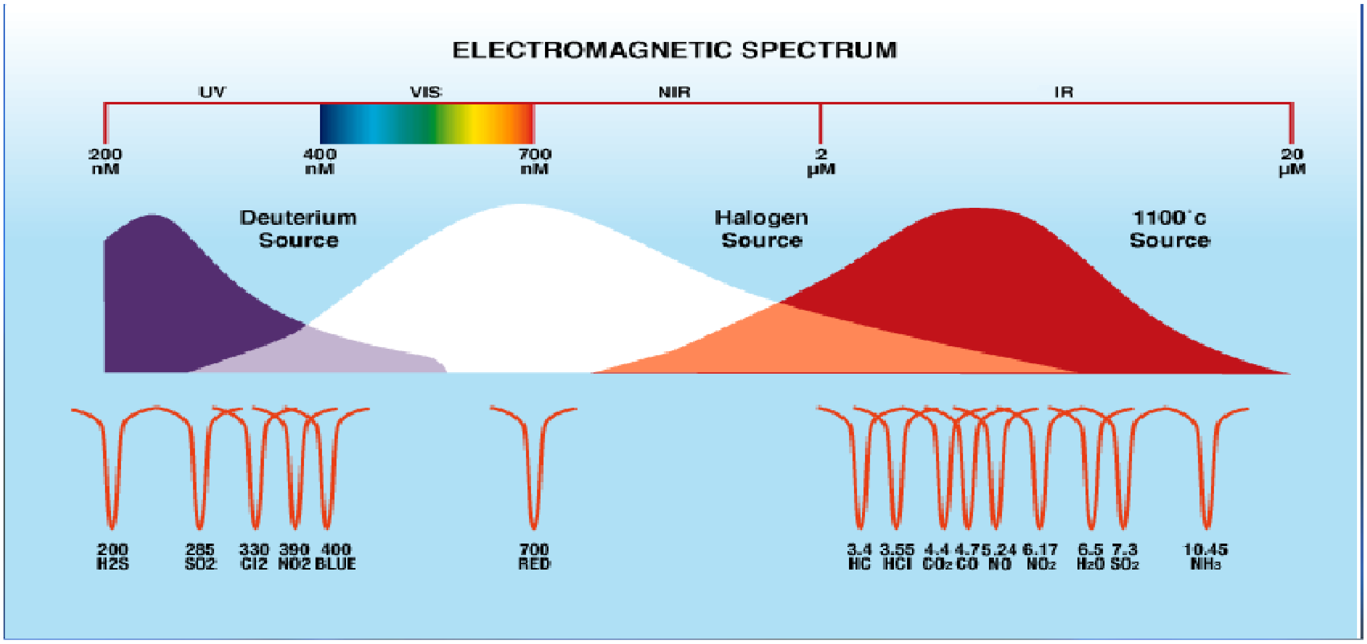



Figure 6.5: The electromagnetic spectrum of light.

# Operation principles of $O_3$ instruments

UV spectroscopy in $O_3$ measurement is the excitation of $O_3$ molecules by using ultraviolet light, specifically from a Mercury lamp. The lamp emits UV light at a wavelength of 254 nm and this is absorbed by an $O_3$ molecule which in turn exites the $O_3$ molecule so that the molecule enters a different energy state.

The detector that is used in $O_3$ analysers is called a UV photometer which detects the UV light at a wavelength of 254 nm and can subsequently detect the amount of absorption that takes place within the sample cell. Using this simple method of only a UV photometer and a glass tube the instrument can accurately detect the amount of $O_3$ that is present in the sample tube by measuring the residual light after absorption has occurred.

Taking all of the above information into consideration we can measure $O_3$ molecules in air.

1. The light source emits UV radiation at a set wavelength of 254 nm which is used to excite the $O_3$ molecules in the sample so that the UV radiation is absorbed by the molecules.
2. The photometer constantly measures the intensity of the UV lamp and when $O_3$ molecules enter the absorption tube the intensity of the radiation from the lamp will be lower due to the absorption of UV radiation by the $O_3$ molecules.

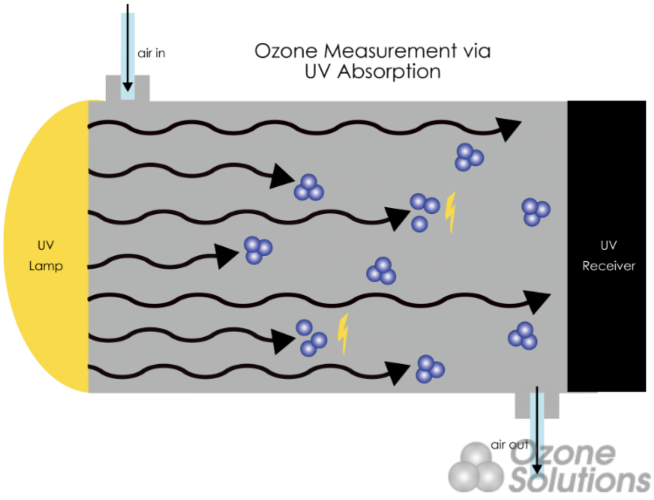



Figure 6.6: Operation principle of $O_3$ analysers.

# Examples of $O_3$ instruments

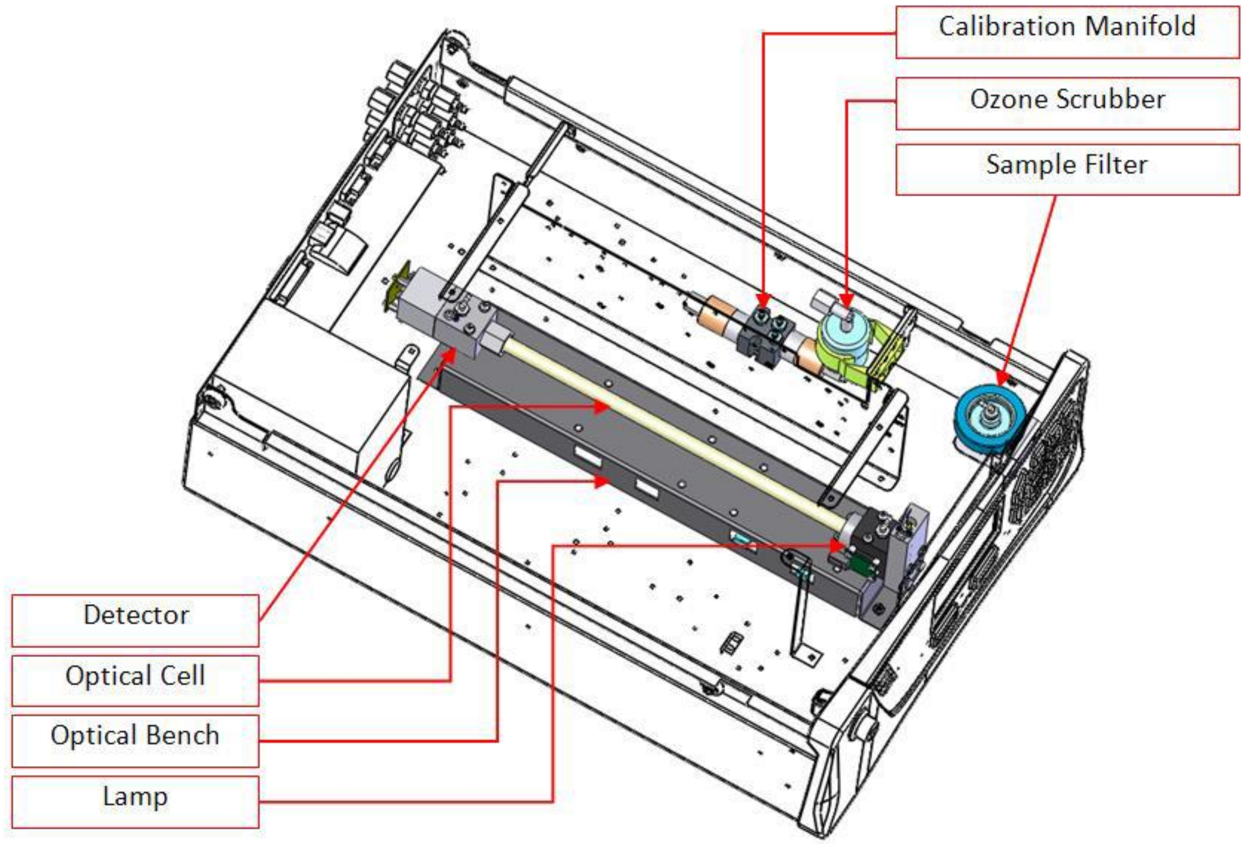



Figure 6.7: Example of the Ecotech Serinus 10 $O_3$ analyser.

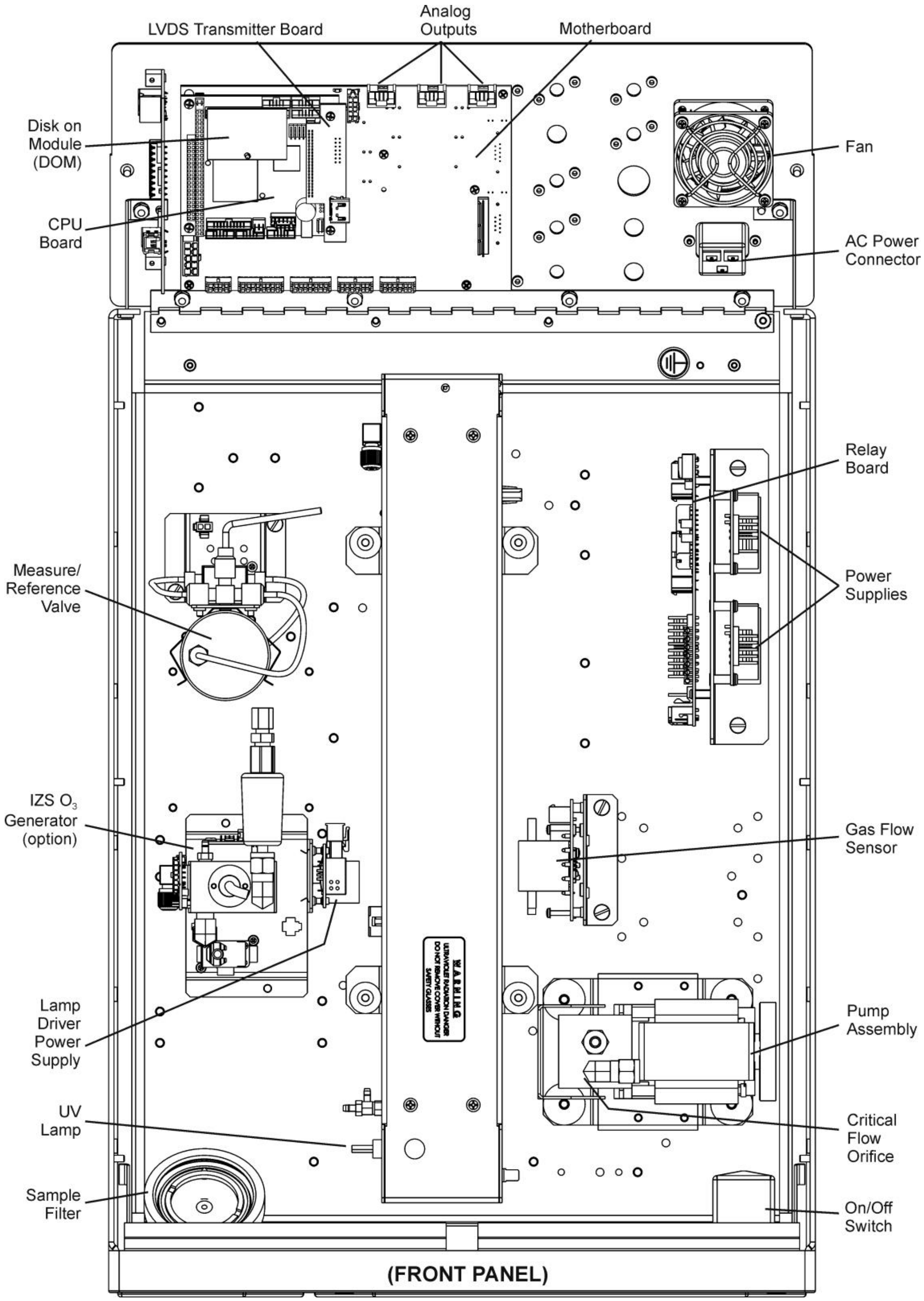



Figure 6.8: Example of API Teledyne T100 $O_3$ analyser.

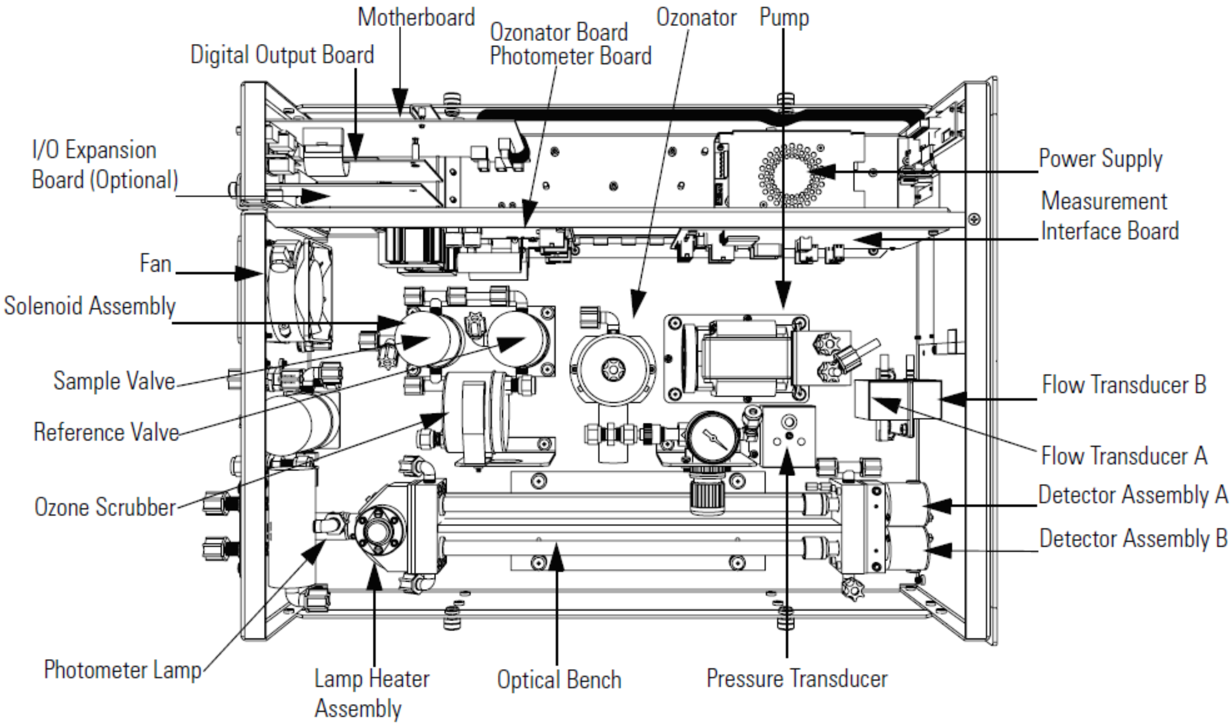



Figure 6.9: Example of Thermo Scientific $O_3$ analyser.

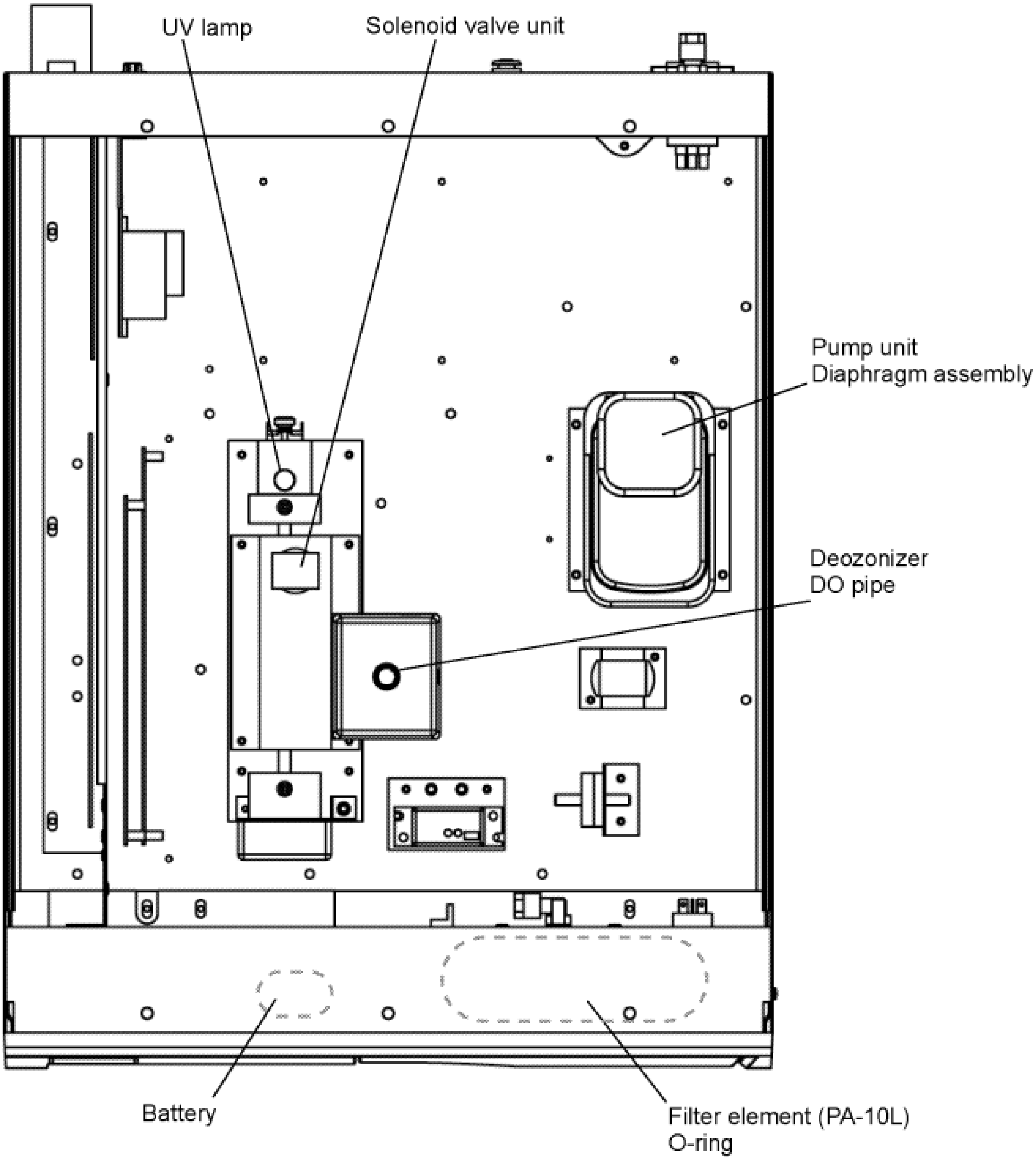
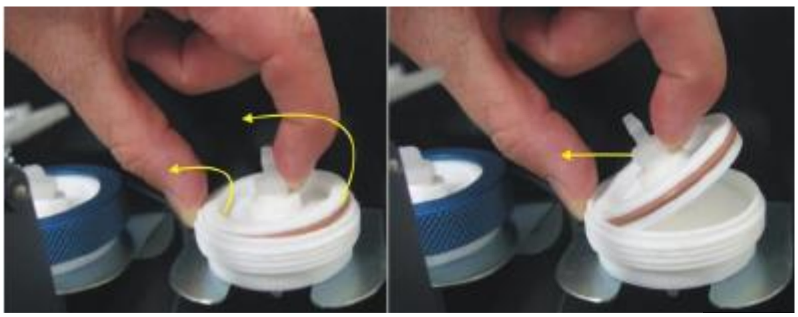


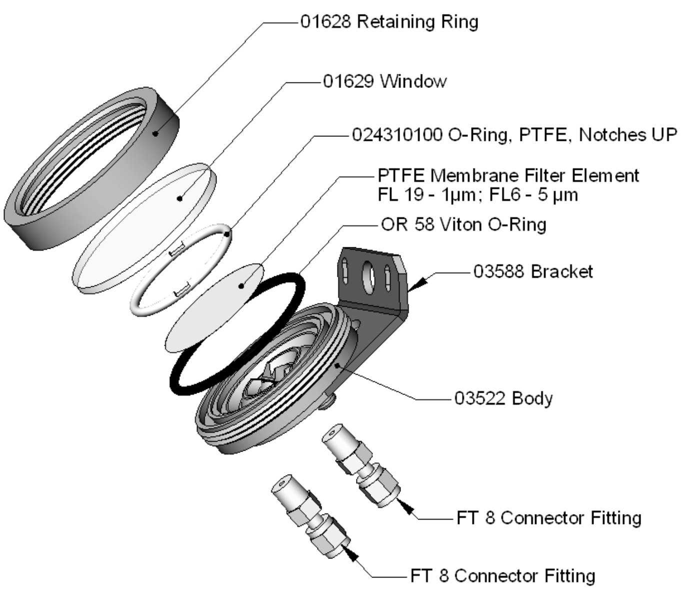

Figure 6.10: Example of Horiba APOA370 $O_3$ analyser.

# Internal components of $O_3$ instruments

From the above examples several different internal components of the $SO_2$ instruments are shown, these internal components are used to ensure that the sample is delivered to the reaction chamber and that any impurities is scrubbed from the sample. Some of the internal components are discussed in further detail below.

## Particulate filter






- All instruments will have a particulate filter. The filter is used to prevent contamination of the internal components of the instrument.
- Contamination of the filter can result in degrading of the instrument performance, including
  - Slow response time (Lower flow)
  - Erroneous readings (Cell contamination)
  - Temperature drift

Figure 6.11: Examples of particulate filters used in an $O_3$ analyser.

## Valve block (Manifold)

During sampling or calibration of the instrument the flow of air needs to be redirected for a specific mode of operation. Valve blocks fitted with small electronic valves are used to control the flow of air as indicated by the user. The valve block can also be referred to as the zero/span/sample control block.

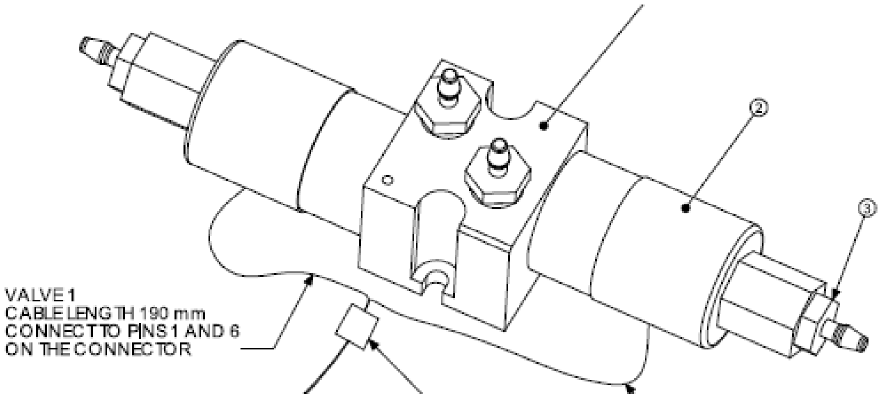
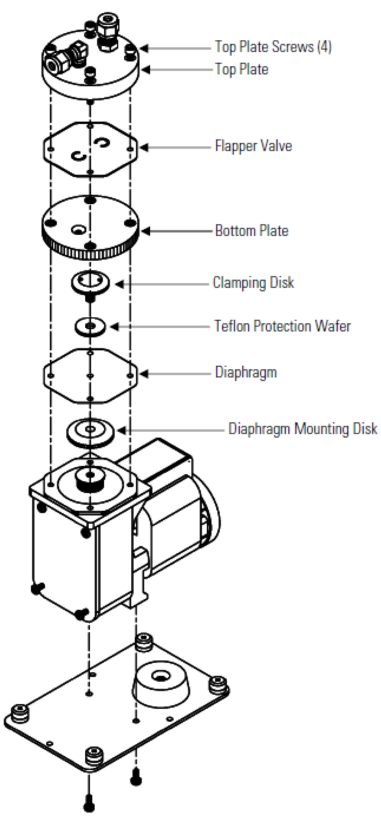



Figure 6.12: Example of valve block used in an $O_3$ analyser.

## Pump




- All instruments require a source of flow to provide a sample to the reaction chamber. For this purpose a pump is used to draw a sample through the instrument.
- A pump can either be built into the instrument or be external and connected to the exhaust port.
- All gas instrument pumps are diaphragm pumps. Meaning a small piston pushes against a diaphragm creating a vacuum thus generating suction.

Figure 6.13: Example of a pump used to draw air through an $O_3$ analyser.

## Ozone scrubber

**Definition**
Ozone scrubbers uses manganese dioxide to scrub the ozone from the sample, providing a reference zero for the other channel.

The ozone scrubber uses manganese dioxide (MnO2) to selectively destroy ozone in the sample air. This leaves the interfering ozone from reaching the optical cell and absorbing the UV radiation. This is performed by a manifold valve which periodically switches between the normal sample and a sample with no $O_3$ molecules to constantly provide a reference of the UV radiation being emitted by the Mercury lamp.

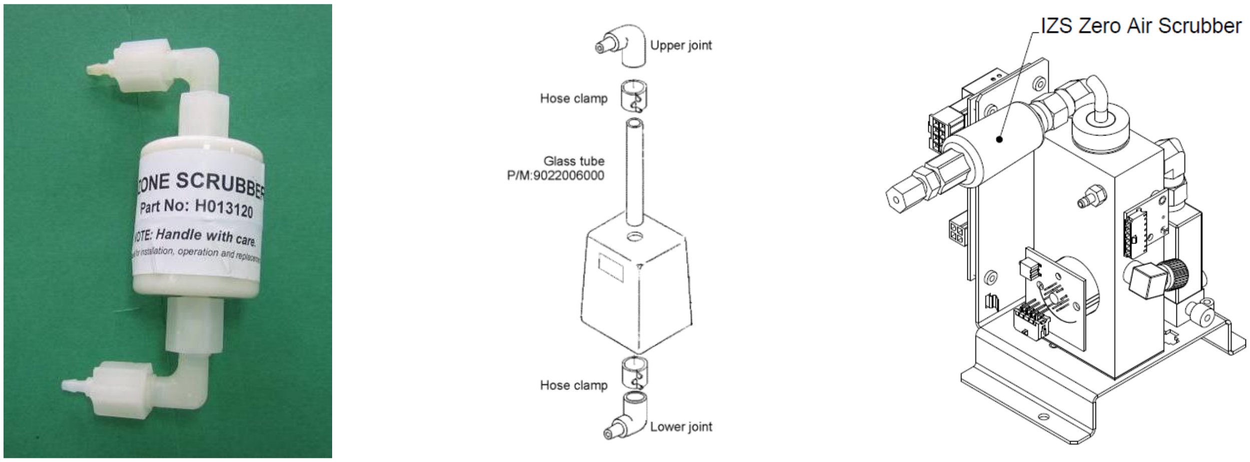



Figure 6.14: Examples of Ozone scrubbers used in an $O_3$ analyser.

## Optical bench

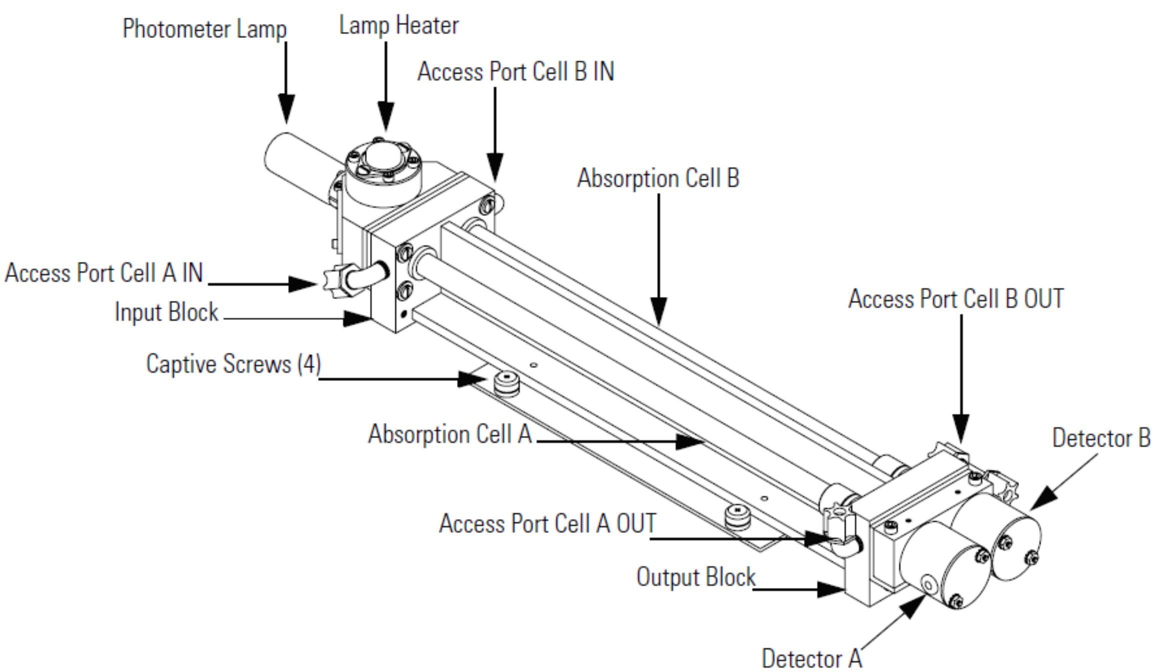



Figure 6.15: Example of the optical bench on an $O_3$ analyser.

The optical bench is where the UV spectroscopy takes place and where the measurement of the sample is performed, the reaction cell is usually made up of six main components:

1. Optical cell
2. UV Source
3. UV Detector

## Optical cell

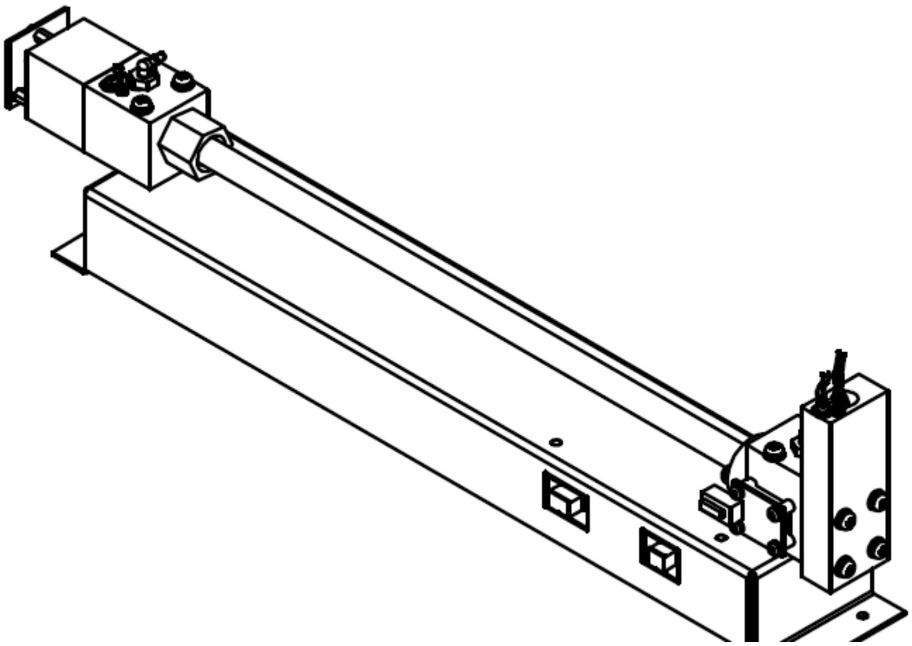


Figure 6.16: Example of the optical cell on an $O_3$ analyser.

This is the optical cell where the UV light at 254 nm is absorbed by the $O_3$ molecules inside the optical cell, the UV photometer can then accurately measure the amount of absorption that takes place by comparing the current reading from the photometer to the reference voltage saved in the memory of the sintrument. The analyser periodically (normally every 6 seconds) switches between the reference sample and the normal sample.

$$O_3 + UV_{254nm} \rightarrow O_3^*$$

$O_3^*$ = Excited $O_3$ (cannot be measured by the photometer)

## Light source (UV-lamp)

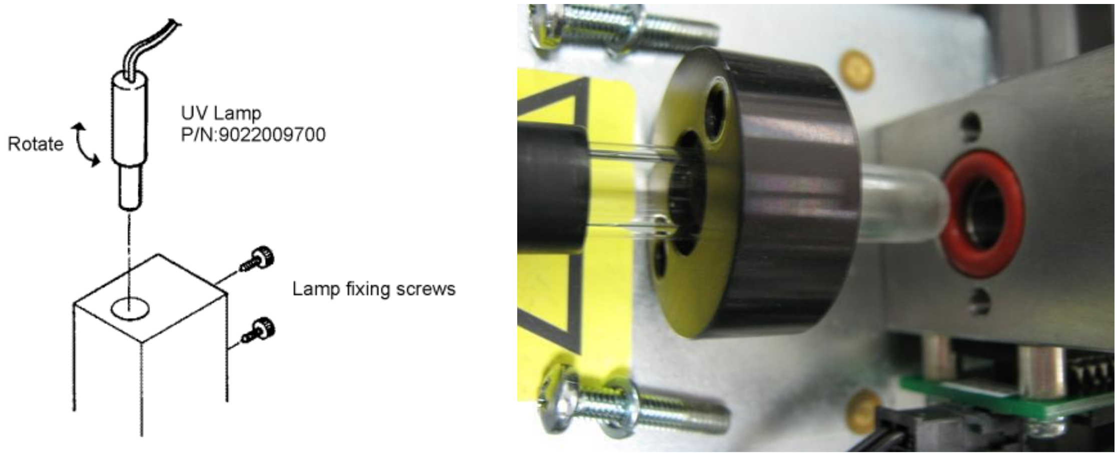



Figure 6.17: Example of the UV-lamp sources used in an $O_3$ analyser.

The light source used in $O_3$ analysers is a mercury lamp which emits UV light/radiation at a known wavelength of 254 nm.

Lamp position: the lamp output is not even across the length of the lamp and can be adjusted for optimal performance.

## UV reference detector

The UV detector used in $O_3$ analysers is a vacuum diode than can only measure UV radiation of 254 nm. The mercury lamp which emits UV light/radiation at a known wavelength of 254 nm is directly measured by the UV detector and any radiation that was absorbed by the $O_3$ molecules in the sample cannot be measured, only the residual radiation is measured.

# Flow of an $O_3$ molecule inside the instrument

With the knowledge of the principles of operation and all the internal components used inside an $O_3$ analyser we can piece together the flow of how an $O_3$ molecule is measured.

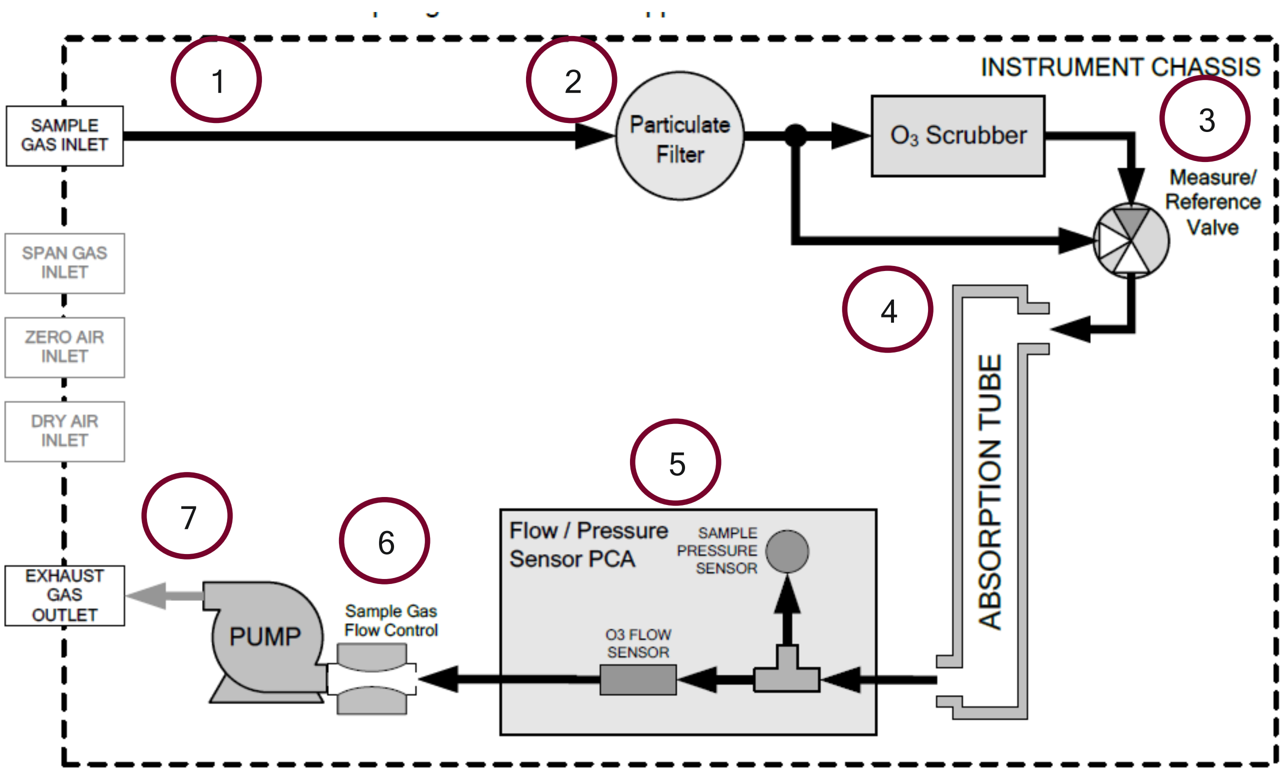



Figure 6.18: Flow process inside an $O_3$ analyser.

1. The sample enters the sample inlet due to the suction created by the pump on the opposite side of the process. The pump is always the final component in the flow process as the pump needs to create a flow of air through the instrument.

2. Once the sample has entered the inlet the sample filter first removes any small dust particles that can influence or contaminate the operation of the instrument.

3. The sample will split and on part of the sample will pass through the Ozone scrubber to scrub any $O_3$ molecules from the sample. This is done to create a reference to which the actual sample containing $O_3$ can be compared to. The reference sample now enters the optical cell where the reference value can be determined.

4. The second part of the sample that contains the $O_3$ molecules can now enter the optical cell where the UV radiation will be absorbed by any $O_3$ molecules that are present in the optical cell. The photometer measure the new radiation after absorption has taken place and can compare the radiation to the reference value previously measured. The amount of $O_3$ is now calculated using these two values.

5. The sample can now exit the optical cell and passes through a flow sensor or pressure sensor to measure the flow of air through the instrument.

6. The next step is the critical orifice inside the manifold which is used to allow the correct amount of air to pass through the instrument.

7. Finally the sample will exit the instrument by being suction created by the pump.

# Maintenance of $O_3$ instruments

Ambient air monitoring instruments are specialized equipment and just like a car these instruments require regular checks and maintenance to ensure that it continues to operate and to ensure the accuracy of measurements and reliability of instrumentation. Table 6.1 provides a schedule of the maintenance and likely repairs that can be performed on an $O_3$ analyser.

| Item | Action | Frequency |
| --- | --- | --- |
| **Particulate Filter** | **Change** | **Bi-Weekly or sooner** |
| **Diagnostic Checks** | **Evaluate** | **Bi-Weekly** |
| **Zero/Span Checks** | **Evaluate** | **Bi-Weekly** |
| **Multi-point calibration** | **Calibrate and verify** | **Every 3 months** |
| Ozone Scrubber | Replace | Annually if required |
| UV Source | Replace | Annually if required |
| Pump | Rebuild Head | If flow drops below instrument operational norms |
| Pneumatics | Clean | Annually if required |
| Reaction Cell | Clean | Annually if required |

Table 6.1: Maintenance and repair schedule.

From table 6.1 the three most important maintenance items are mentioned first with the most important maintenance item being the changing the particulate filter every two weeks.

The particulate filter ensures that no dust or debris enters the instrument as this can contaminate the lenses, optical filters and sensors which will affect the operation of the instrument. Always make sure to change the operating mode of the instrument or switch of the pump when replacing the particulate filter, this way no fine particulates can enter the instrument while changing out the filter. Refer to figure 6.11.

The second important item to check is the diagnostics of the instrument, these are the parameters of the measurements of internal control systems that are in place to ensure optimal operation of the instrument. Most instruments will display a warning on the screen of the instrument if there are any of the parameters that are not within the specified range but it is also important to check all the parameters every two weeks to ensure there were no major changes in any if the parameters.

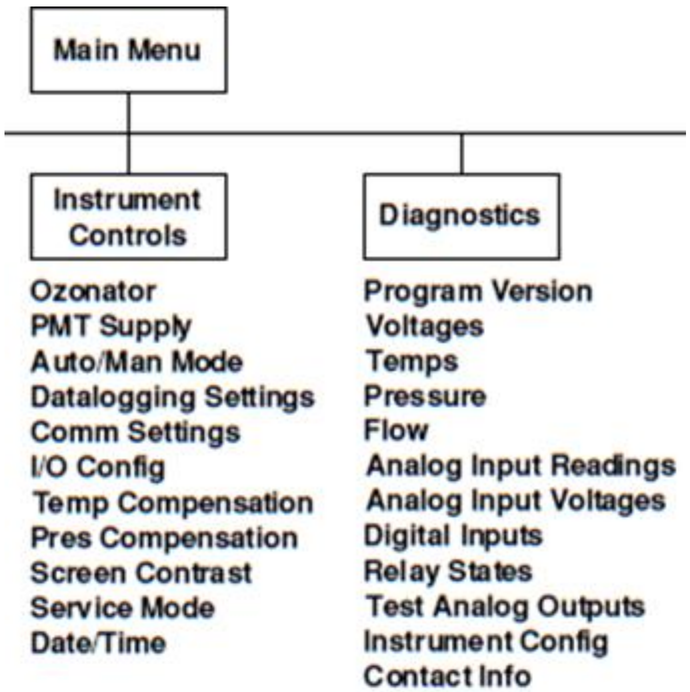



Figure 6.19: Example of instrument menu to check system diagnostics.

| O₃ API Analyser | | | |
|---|---|---|---|
| Manufacturer | API | Station Name: HAMMANSKRAAL | |
| Model Number | M400E/T400 | Operator Name: CORNÉ GROVÉ | |
| Serial Number | 3082 | Date: 6/12/2017 | |

**Diagnostics check sheet**

| $O_3$ Parameters | Nominal value / range (1) | Observed (2) | Value 1=2 (Y/N) | Deviation |
|---|---|---|---|---|
| Range (ppb) | 50 – 500 ppb | | | |
| Stability | 0.02 - 2 | 0,31. | | |
| O3 Measure mV | 2500 – 4800 | 3482,3 | | |
| O3 Ref mV | 2500 – 4800 | 3482,3 | | |
| O3 Gen mV | 80 – 5000 | 613,1 | | |
| O3 Drive mV | - | 1029,9 | | |
| Sample Pressure IN-HG-A | ~2" < Ambient | 24,4 | | |
| Sample Flow cc/min | 800 ± 10% | 783,5 | | |
| Sample Temperature | 10 – 50 °C | 39,7 | | |
| Photo Temperature | 58 ± 1 °C | 58,0 | | |
| O3 Gen Temperature | 48 ± 3 °C | 48,0 | | |
| Box Temperature | 10 – 50 °C | 26,8 | | |
| Slope | 1 ± 0.3 | 1,192 | | |
| Offset ppb | 0.0 ± 5.0 | -2,3. | | |
| Instrument Faults | | 0 | | |

Figure 6.20: Example of instrument diagnostics that were recorded.

https://en.wikipedia.org/wiki/Ozone

https://en.wikipedia.org/wiki/Frequency